Development and Optimization of Multi-Functional SCR-DPF Aftertreatment for Heavy-Duty NOx and Soot Emission Reduction

KENNETH RAPPÉ, BO PENG, YONG WANG, FENG GAO, JANOS SZANYI
Pacific Northwest National Laboratory

2018 Annual Merit Review, DOE Vehicle Technologies Office
Arlington, VA
June 20, 2018

Project ID: ACS119

Overview

Timeline

- 4-yr CRADA
  - Start date – July 2016
  - End date – June 2020
- 41.7% complete

Barriers

- **B. Lack of cost-effective emission control** for meeting EPA standards for NOx & PM
- **E. Durability** of the emission control system: 435,000 miles
- **G. Cost** of emission control devices … for heavy duty engines in particular

Budget

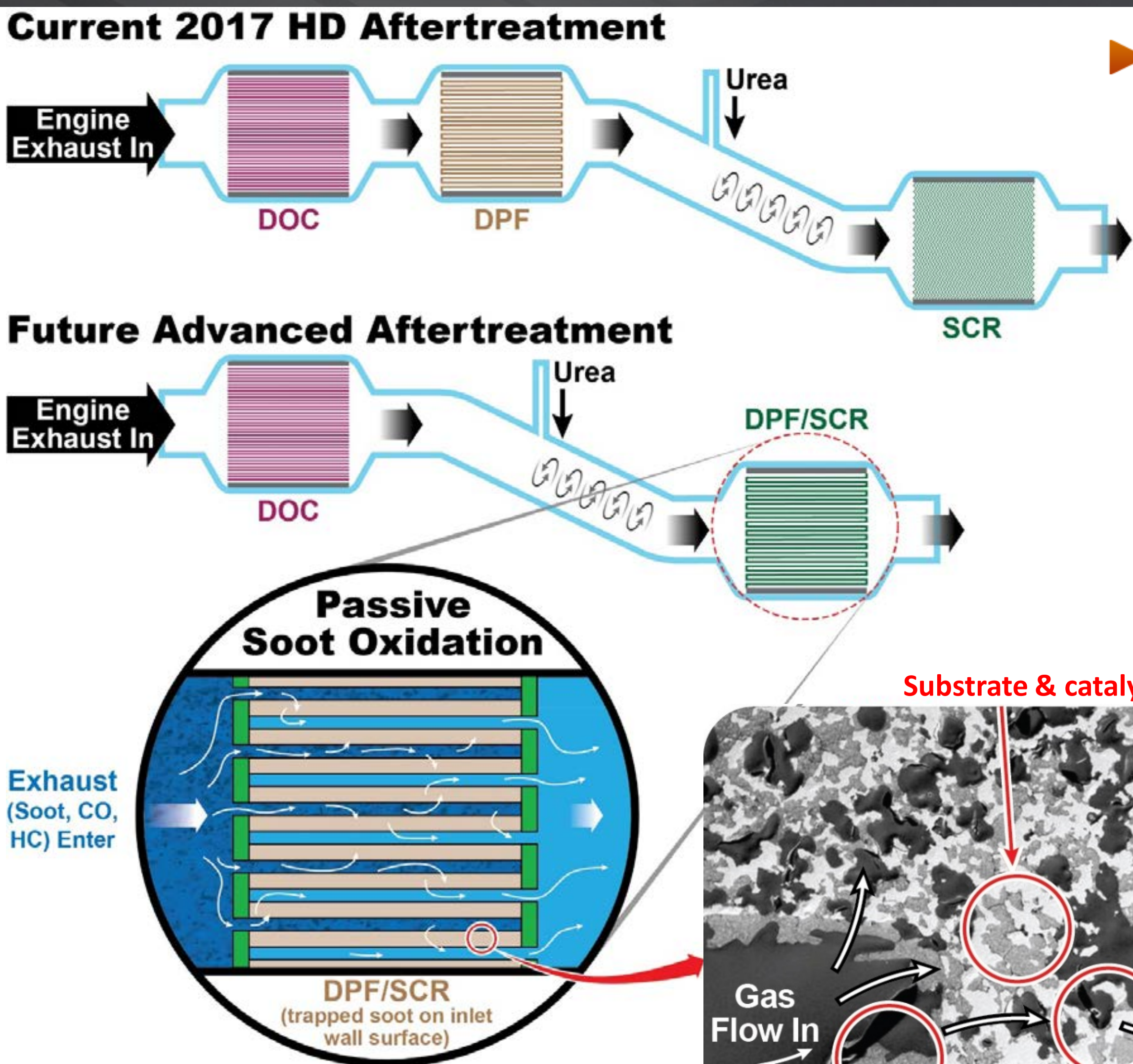
- Contract value – $2.7M
  - $1.35M DOE share
  - $1.35M PACCAR share
- Funding received
  - FY16 – $200K
  - FY17 – $355K
  - FY18 – $175K

Partners

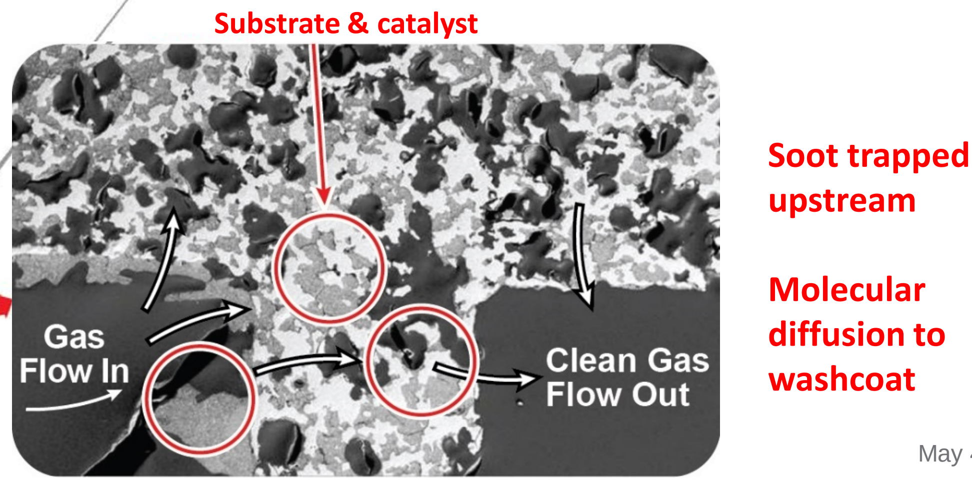
PACCAR Inc

- CRADA partner

Relevance
Multi-Functional Aftertreatment: SCR-on-DPF



- Highly promising strategy of integration
  - Reduced total thermal mass of aftertreatment system
    - *Faster warm up*
    - *Reduced cold start emissions*
  - Improved performance & increased flexibility
    - *SCR closely coupled to engine*
    - *Increased SCR volume*



Relevance
SCR-on-DPF (for heavy duty application)

Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by Battelle *Since 1965*

- Challenges to deployment

1. SCR catalyst performance – light/heavy duty
   - ❑ Enablers – ultra-high porosity filter development, advanced imaging techniques

2. SCR catalyst durability – light/heavy duty
   - ❑ Enablers – small-pore Cu-zeolites, e.g., Cu/SSZ-13. more thermally durable

3. **Passive soot oxidation performance (via NO_2) – heavy duty**
   - ❑ Economically attractive to manage soot passively for heavy duty
   - ❑ With incorporation of SCR phase, *competition for NO_2*

Fast-SCR

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O$$

Dominates NO_2 consumption

versus

Significantly compromises soot oxidation

Passive soot oxidation

$$C\ (soot) + 2NO_2 \rightarrow CO_2 + 2NO$$

Approach

Modify the SCR catalyst to generate NO_2 in situ

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by **Battelle** *Since 1965*

- Focus – Incorporating *increased NO oxidation (to NO_2)* through inclusion of a metal-oxide component for selective catalytic oxidation (SCO)
  - i.e. forming an SCR-SCO binary catalyst system (as a single active phase)

PROJECT OBJECTIVES

- **NO oxidation**
  - Target: increased NO oxidation to NO_2
  - … that then drives increased passive soot oxidation
- **SCR catalyst performance [i.e., NOx reduction efficiency (NRE)]**
  - Target: NO oxidation without oxidizing NH_3
  - Target: NRE ≥ current state-of-the-art (Cu-CHA)
- **SCR catalyst durability**
  - Target: durability ≥ current state-of-the-art (Cu-CHA)

Must develop in *integrated* fashion

Approach

Modify the SCR catalyst to generate NO_2 in situ

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle *Since 1965*

- Focus – Incorporating ***increased NO oxidation (to NO_2)*** through inclusion of a metal-oxide component for selective catalytic oxidation (SCO)

PROJECT OBJECTIVES this past year

- **NO oxidation – PACCAR focus**
- **SCR catalyst performance and durability – PNNL focus**
  - **Step 1 – SCO substrate**
    - SCO is envisioned as a ZrO_2-based catalyst
    - Understanding the impact of ZrO_2 in close proximity to the SCR catalyst
    - … including the impact on both SCR performance and durability
  - **Step 2 – SCO catalyst**
    - Impact of hetero-atoms included with ZrO_2
      - Inside the lattice structure, outside the lattice structure, etc.
    - Including their impact on SCR performance and durability

Approach

Schedule and Milestones

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by **Battelle** *Since 1965*

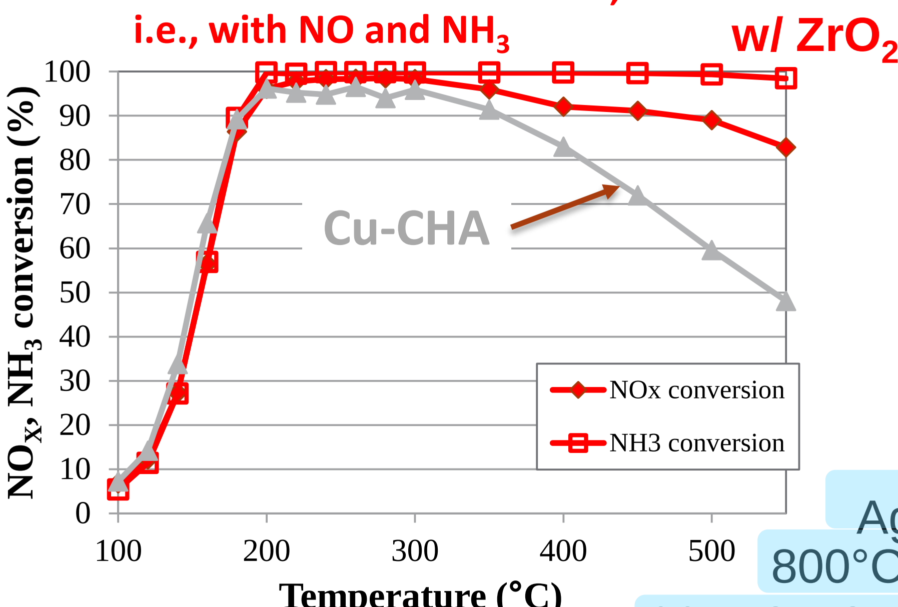
Date*	Milestone and Go/No-Go Decisions	Status
November 2017	Milestone: 1st group of optimized SCRF samples with candidate SCO/SCR binary catalyst ready for detailed testing	Complete
February 2018	Go/No-Go decision: Identify candidate SCO/SCR binary phase catalyst with improved soot oxidation performance with competing SCR	Delayed
February 2018	Milestone: Composition for first increased scale testing	Complete (PACCAR)
May 2018	Milestone: 2nd group of optimized SCRF samples with candidate SCO/SCR binary catalyst ready for detailed testing	On-track
August 2018	Milestone: SCRF single wall model complete (without aging behavior)	In pursuit
August 2018	Milestone: Production of catalyst for first increased scale testing	Complete

Accomplishments
SCR catalyst performance and durability

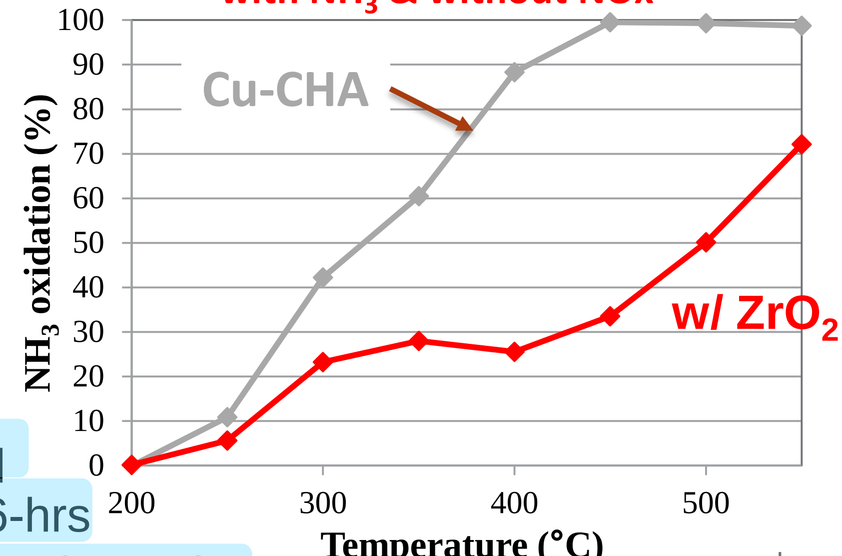
Pacific Northwest NATIONAL LABORATORY
Proudly Operated by **Battelle** *Since 1965*

- ZrO_2-based metal-oxide SCO catalyst
  - Focus – Understanding the impact of ZrO_2 on SCR performance and durability
  - Baseline – Cu-CHA (Si/Al = 12, Cu ~2.3 wt%, IE level ~30%)
- ***ZrO_2 addition leads to significantly improved high temperature selectivity by mitigating NH_3 oxidation***

Standard SCR reaction conditions, i.e., with NO and NH_3



NH_3 oxidation conditions, i.e., with NH_3 & without NOx

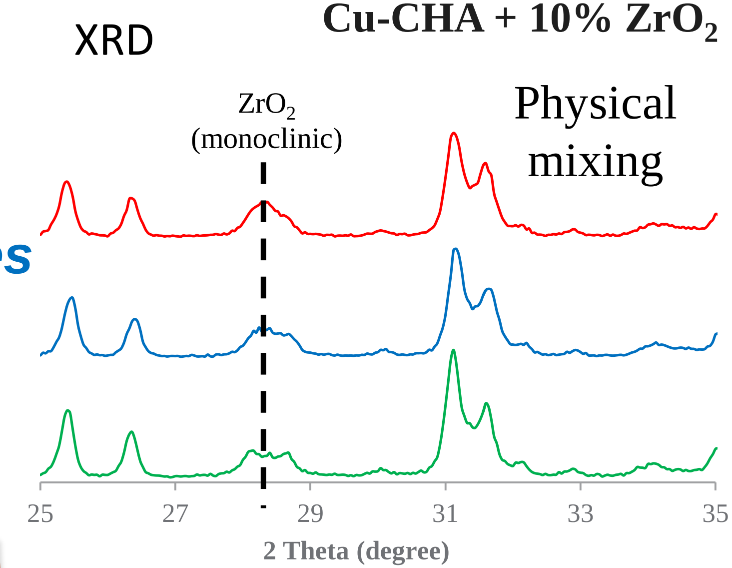


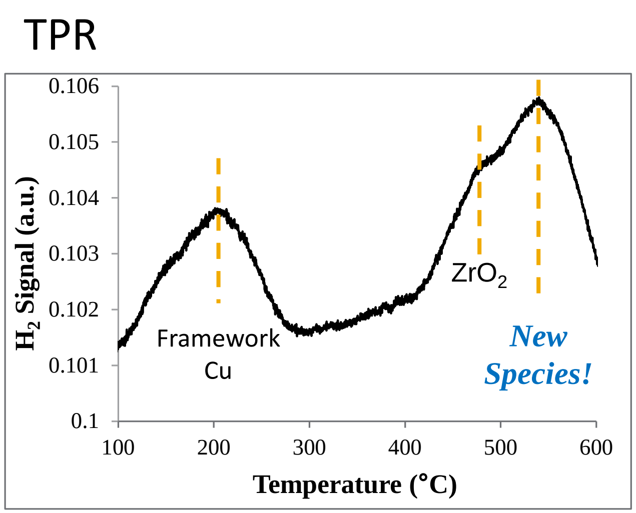
Aged
800°C/16-hrs
90% Cu-CHA + 10% ZrO_2

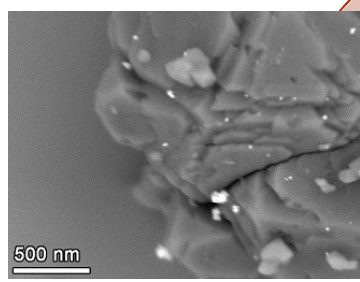
Accomplishments
SCR catalyst performance and durability

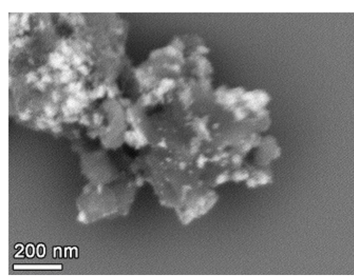
- ZrO_2-based metal-oxide SCO catalyst
  - Focus – Understanding the impact of ZrO_2
- ***Identified the generation of a new species resulting from the interaction between extra-framework Cu (i.e., CuO) and ZrO_2***
- *Closer vicinity = Increased interaction between extra-framework Cu and ZrO_2*

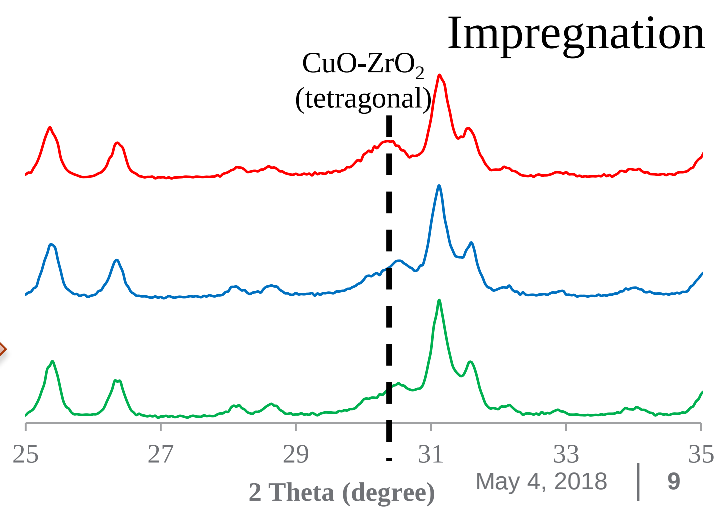
Cu-CHA + 10% ZrO_2







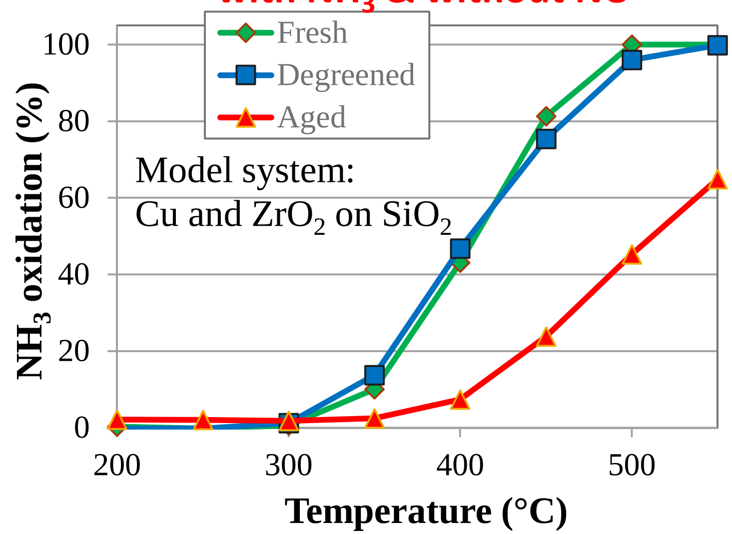




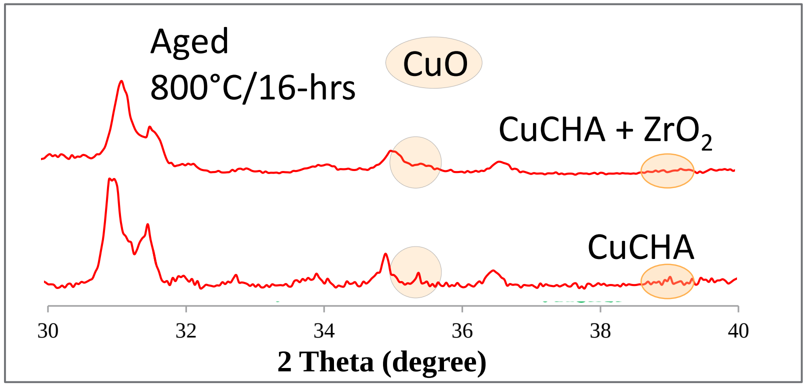
Accomplishments
SCR catalyst performance and durability

- ZrO_2-based metal-oxide SCO catalyst
- *ZrO_2 addition and extra-framework Cu-incorporation as hetero-atom*
- ***Demonstrates the ability to incorporate hetero-atoms into the ZrO_2 matrix (e.g., for improving NO oxidation) while mitigating NH_3 oxidation and the adverse impact on SCR performance, and improved durability***

NH_3 oxidation conditions, i.e., with NH_3 & without NO



XRD



- CuO_x → inferior high-T selectivity

 and

- CuO_x → damages the zeolite

i.e. the worm in apple

Song, et al., ACS Catal., 7-12 (2017) 8214-8227

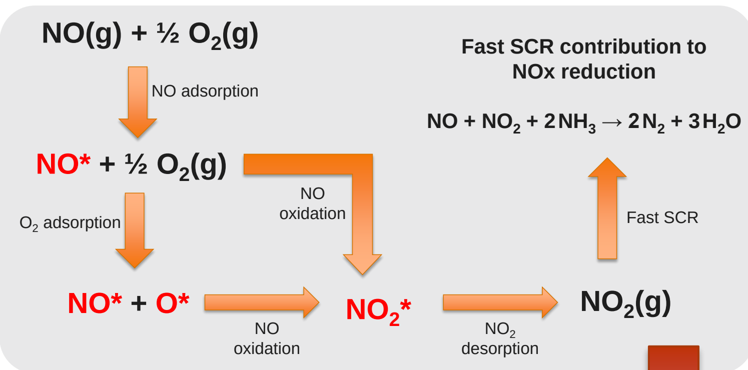
Accomplishments

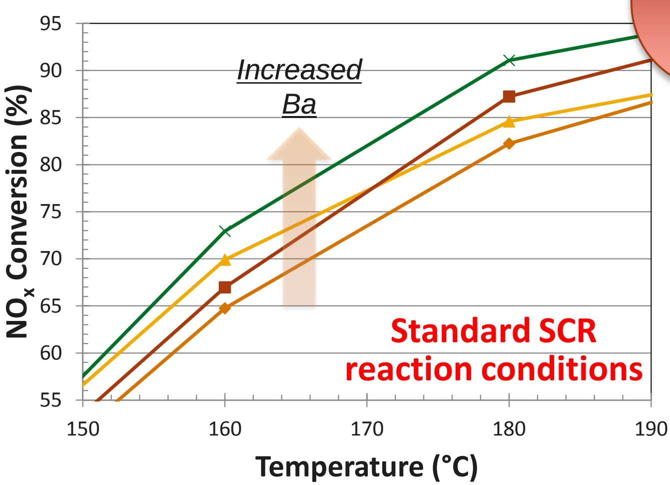
Taking advantage of a NOx storage component

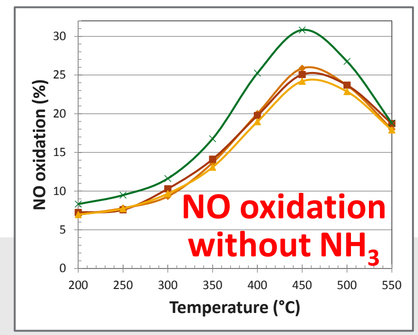
- Including Ba – 90% Cu-CHA + 10% Ba/Zr-oxide

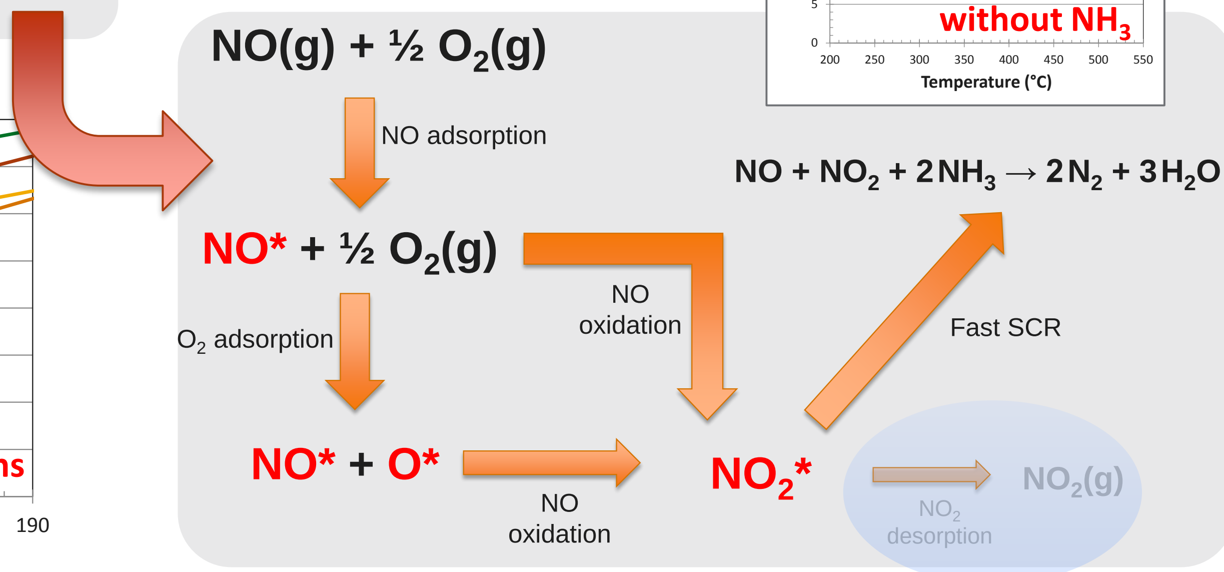
- With Ba, resolving …
  - Analogous NO oxidation activity
  - Increased NOx reduction efficiency

Ba/Zr-oxide shows evidence of the ability to take advantage of a surface-active species





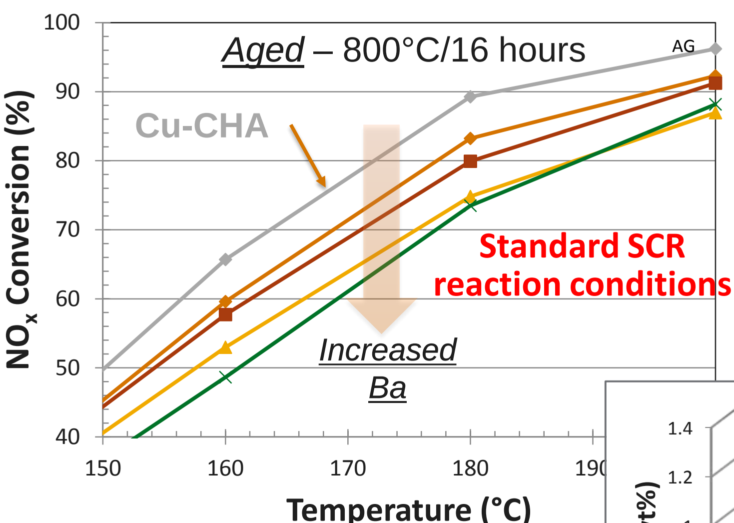


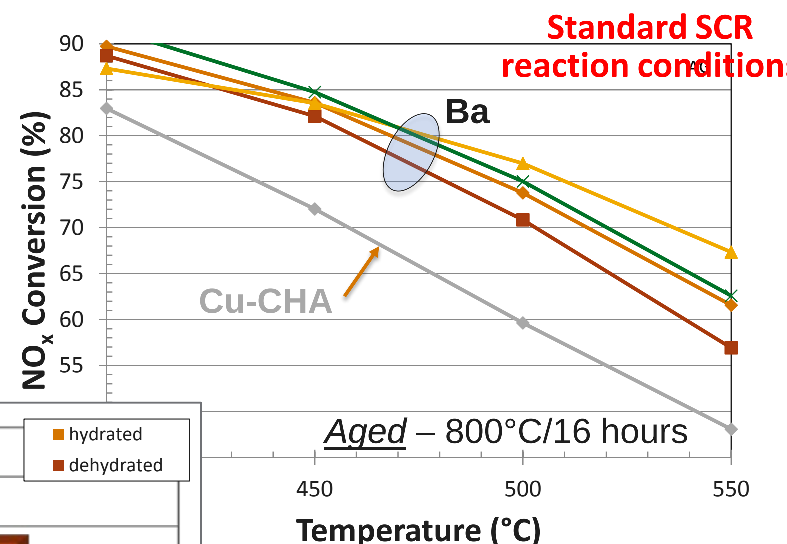


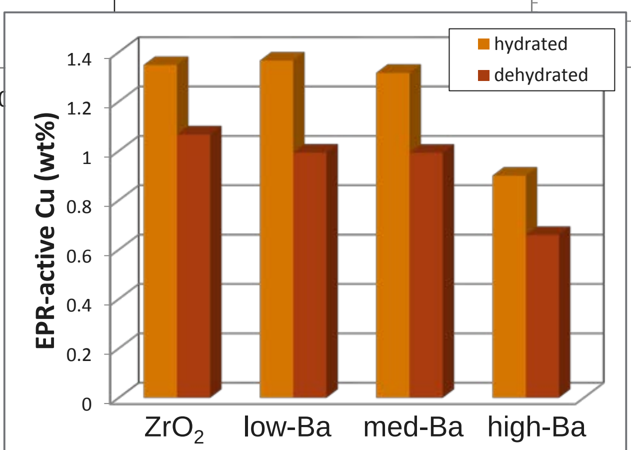
Accomplishments

Implications of Ba on SCR catalyst durability

- Including Ba – 90% Cu-CHA + 10% Ba/Zr-oxide
- ***Work has uncovered an aging mechanism that uniquely affects <u>low-temperature activity</u> of BaO/ZrO_2 versus Cu-CHA or with ZrO_2***







Low Temperature

- *Reduced activity observed*

High Temperature

- *Activity compared to ZrO_2*

Accomplishments
SCR catalyst durability

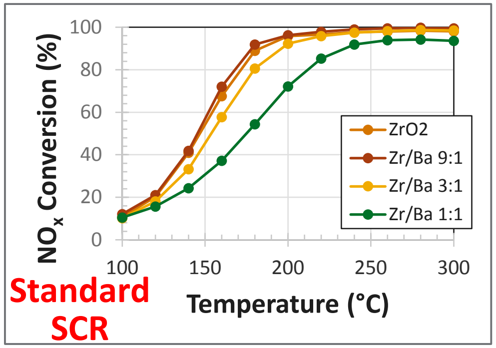
Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

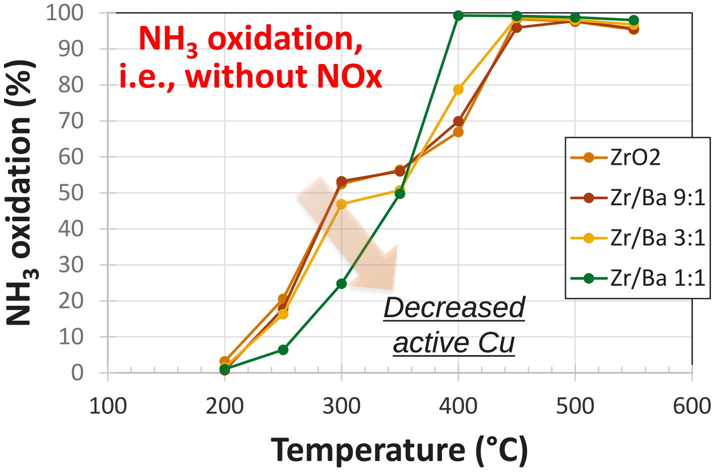
- Including Ba – 90% Cu-CHA + 10% Ba/Zr-oxide
- Thermally-induced ion-exchange aging mechanism
  - = *function* (time, temperature, proximity)

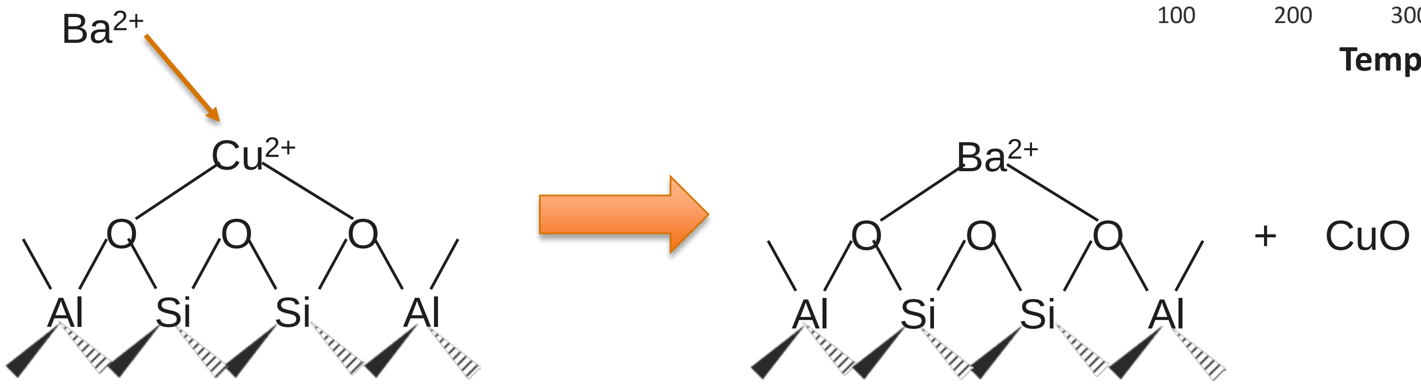
Ion-exchange aging behavior …

- 800°C/16-hrs >> 650°C/100-hrs
- Closer vicinity >> physical mixture

Must be cognizant of aging mechanism in relation to SCO catalyst chemistry AND proximity to SCR phase





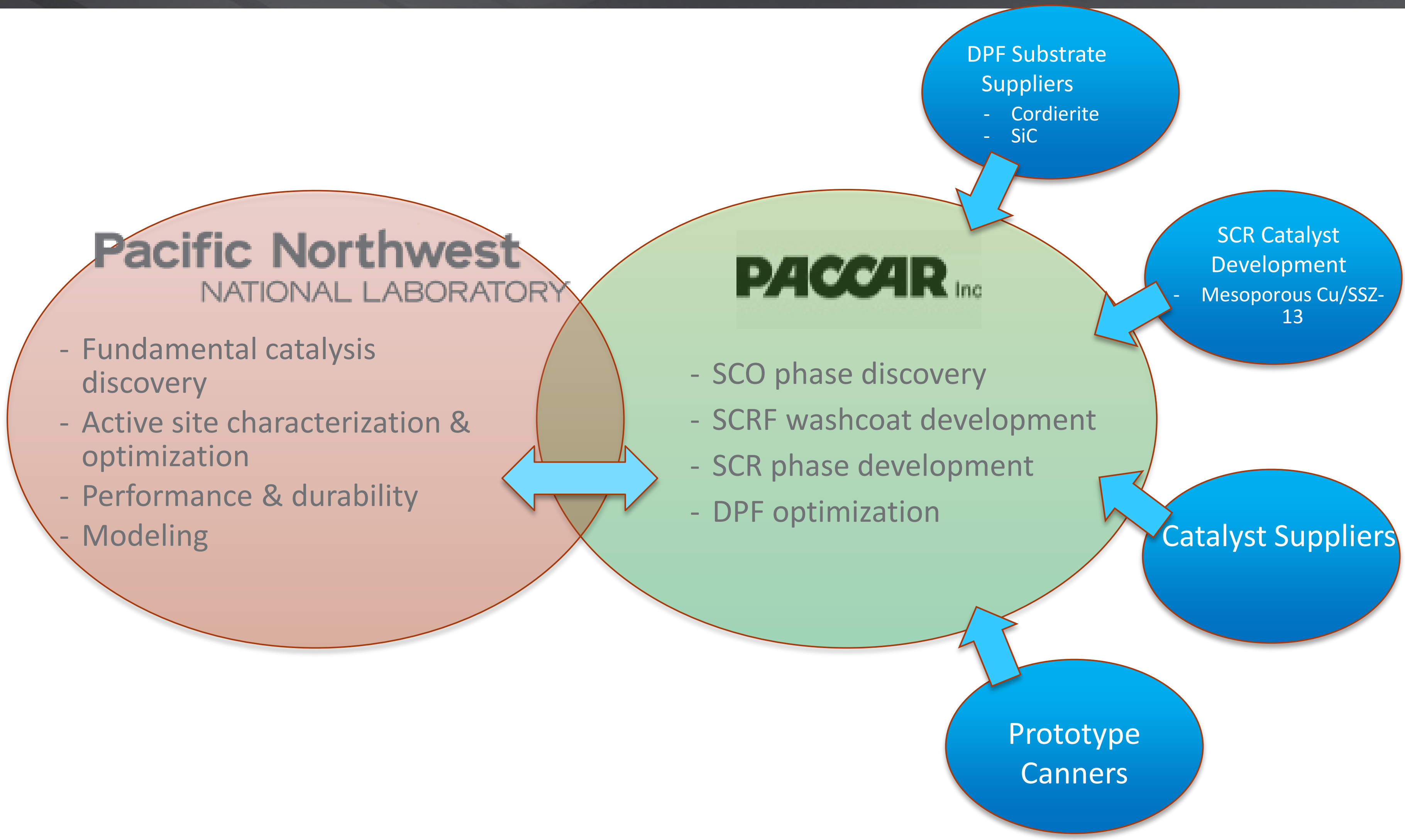


Responses to Previous Years Reviewers' Comments

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

- The reviewer opined that work on ZSM-5 is a waste of time. This reviewer affirmed that moving to SSZ-13 is correct. The reviewer further remarked that the most important part of the project is the durability study, and S effects need to be included.
  - *We agree that durability must be intimately considered in the development. Thus, this has been PNNL emphasis in the past year*
- This reviewer commented that the approach seems naive. This reviewer stated that it will be extremely difficult, if not impossible, to balance high SCR conversion with high soot oxidation.
  - *With current state-of-the-art SCR technology, we do not disagree. Thus, we are trying modify current SCR technology to enable the application. This is the novelty of the work.*
- The reviewer said that work with Cu-ZSM-5 was not relevant. The reviewer noted that it is unclear how the filters are being coated.
  - *ZSM-5 was employed solely as a model system, and we have moved past this stage.*
  - *Filters are being coated by PACCAR*

Collaboration and Coordination



Remaining Challenges and Barriers

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

- **NO oxidation**
  - Increased NO oxidation to NO_2
  - … to drive increased passive soot oxidation
- **NOx reduction efficiency (NRE)**
  - *Increasing NO oxidation without oxidizing NH_3*

Proposed Future Work

- **NO oxidation**
  - Modifying ZrO_2 chemistry (increased redox, acidity)
  - More aggressive active NO oxidation component (e.g., Mn, Co, …)
  - … with and without Ba
- **NOx reduction efficiency (NRE)**
  - Incorporating (Mn, Co, …) into ZrO_2-based lattice
  - Prior work – metals in a support lattice structure (i.e., co-precipitated) can be just as active for NO oxidation versus supported
  - Leveraging this with the ability of ZrO_2 to mitigate NH_3 oxidation activity of hetero-atoms (as shown from extra-framework Cu interaction)

Any proposed future work is subject to change based on funding levels

Summary

- ZrO_2 addition shown to improve performance by interacting with extra-framework Cu (i.e., CuO) and ZrO_2
  - Generation of a new species resulting from the interaction
  - Significantly improved high temperature selectivity by mitigating NH_3 oxidation
  - Closer vicinity = Increased interaction between extra-framework Cu and ZrO_2
- ZrO_2 demonstrates the ability to incorporate hetero-atoms into matrix (e.g., for improving NO oxidation) while mitigating detrimental SCR impact
- Ba/Zr-oxide shows evidence of the ability to take advantage of a surface-active species as a pathway to enhanced NO oxidation behavior
- Uncovered an ion-exchange (IE) aging mechanism that uniquely affects low-temperature activity of BaO/ZrO_2 versus Cu-CHA or with ZrO_2
- Development must be cognizant of IE aging mechanism in relation to SCO catalyst chemistry AND proximity to SCR phase

Technical Backup Slides

KENNETH RAPPÉ, BO PENG, YONG WANG, FENG GAO, JANOS SZANYI

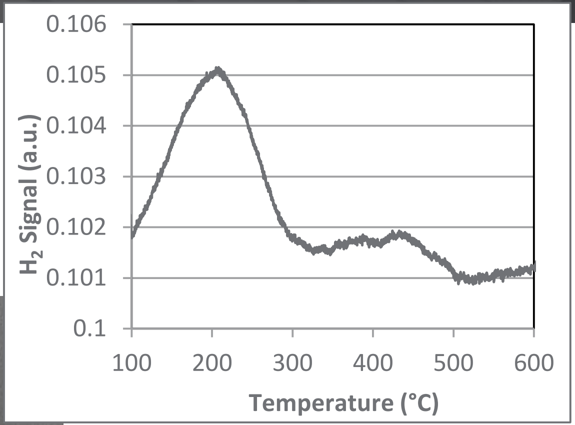
Pacific Northwest National Laboratory

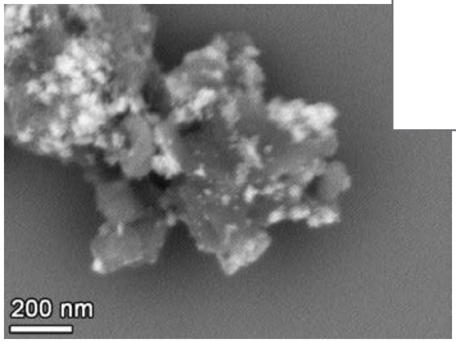
2018 Annual Merit Review, DOE Vehicle Technologies Office
Arlington, VA
June 20, 2018

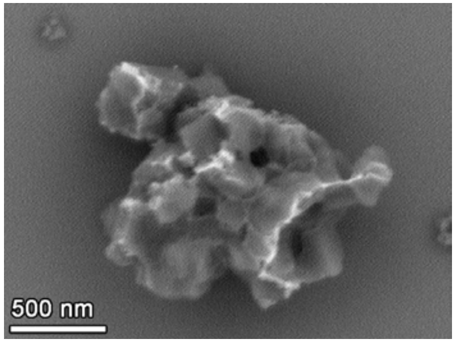
Project ID: ACS119

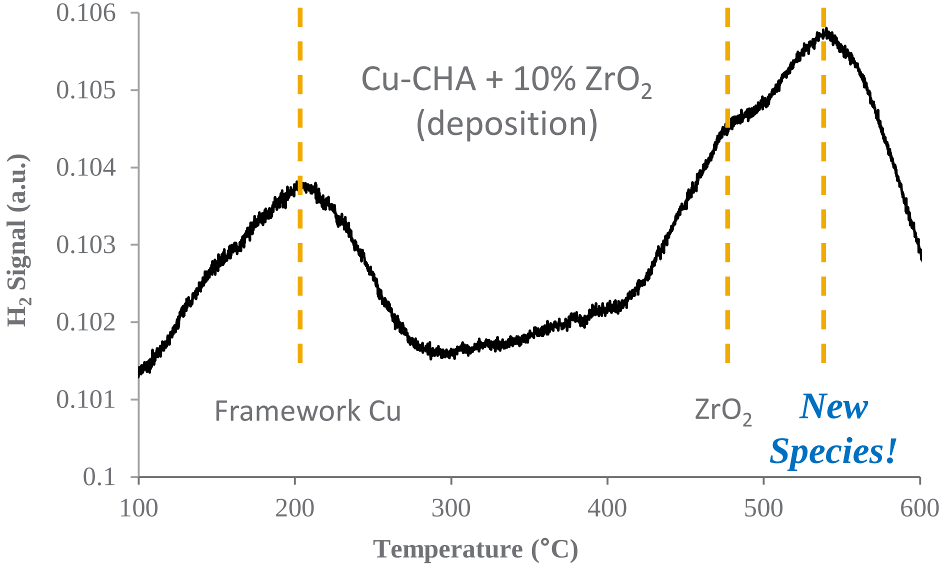
Backup – Enhancing the Cu/ZrO_2 interaction

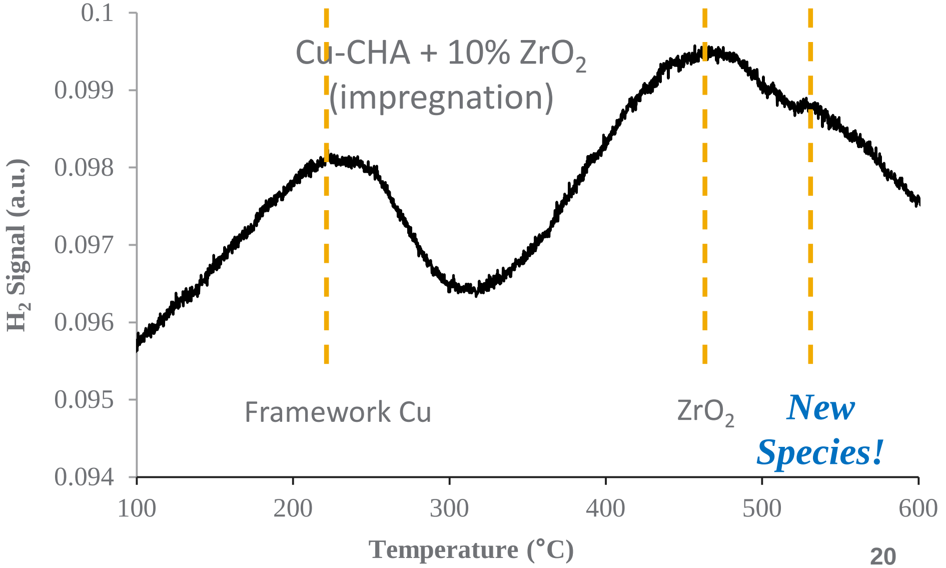
- New species observed in the TPR profile of deposited- and impregnated-ZrO_2 on Cu-CHA





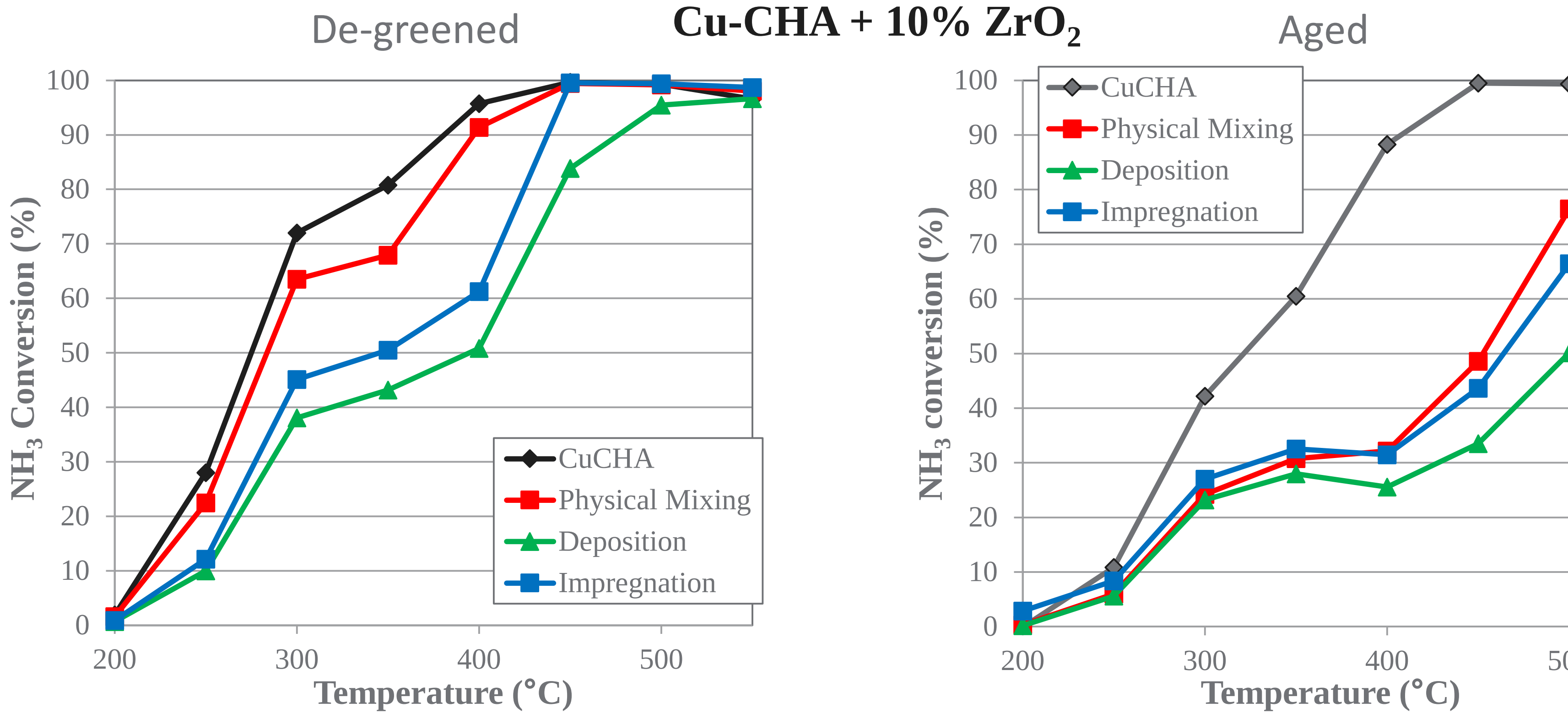






Backup – Reduced NH_3 oxidation (by O_2)

Cu-CHA + 10% ZrO_2

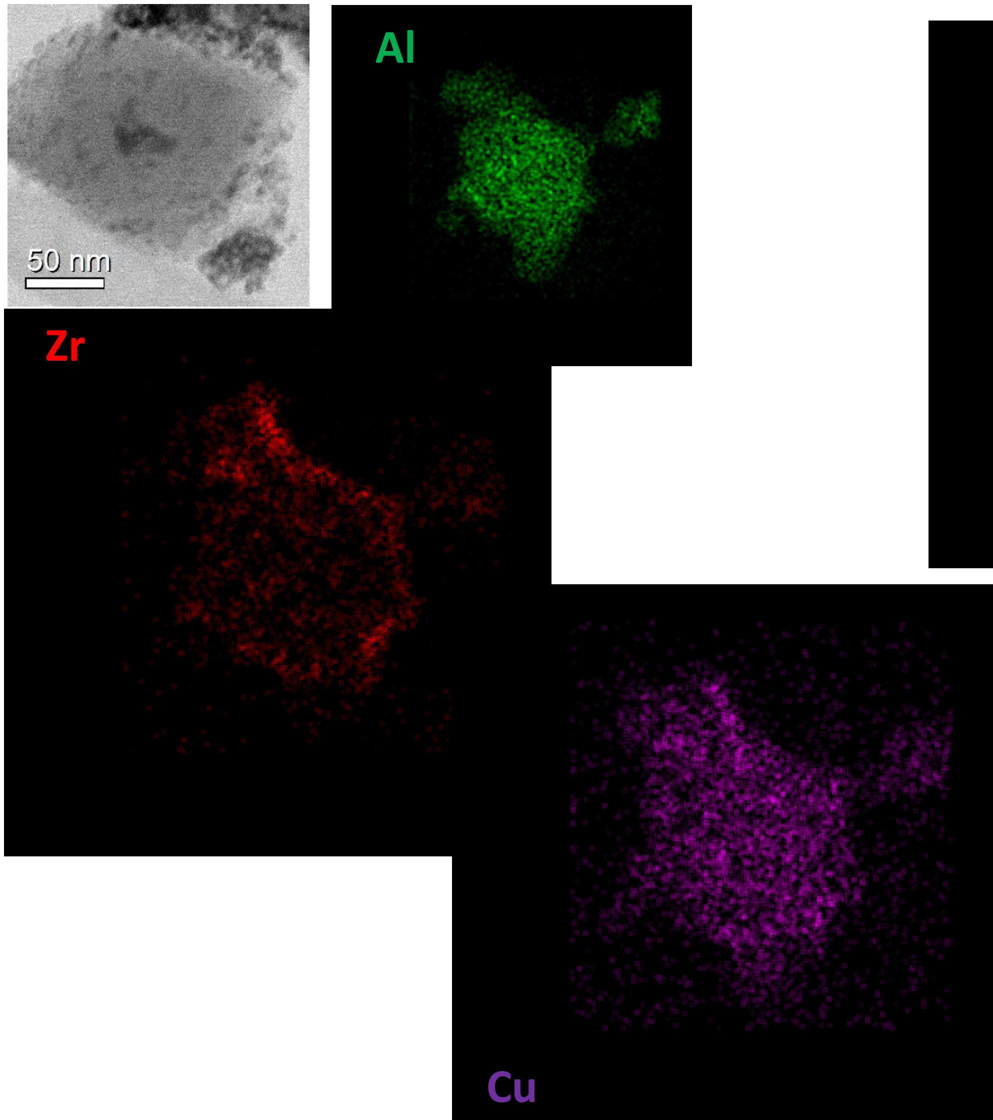


Conditions: 360 ppm NH_3, 14% O_2, 2.5% H_2O, balanced by N_2, total flow rate 300 mL min^{-1}, 120 mg catalyst.

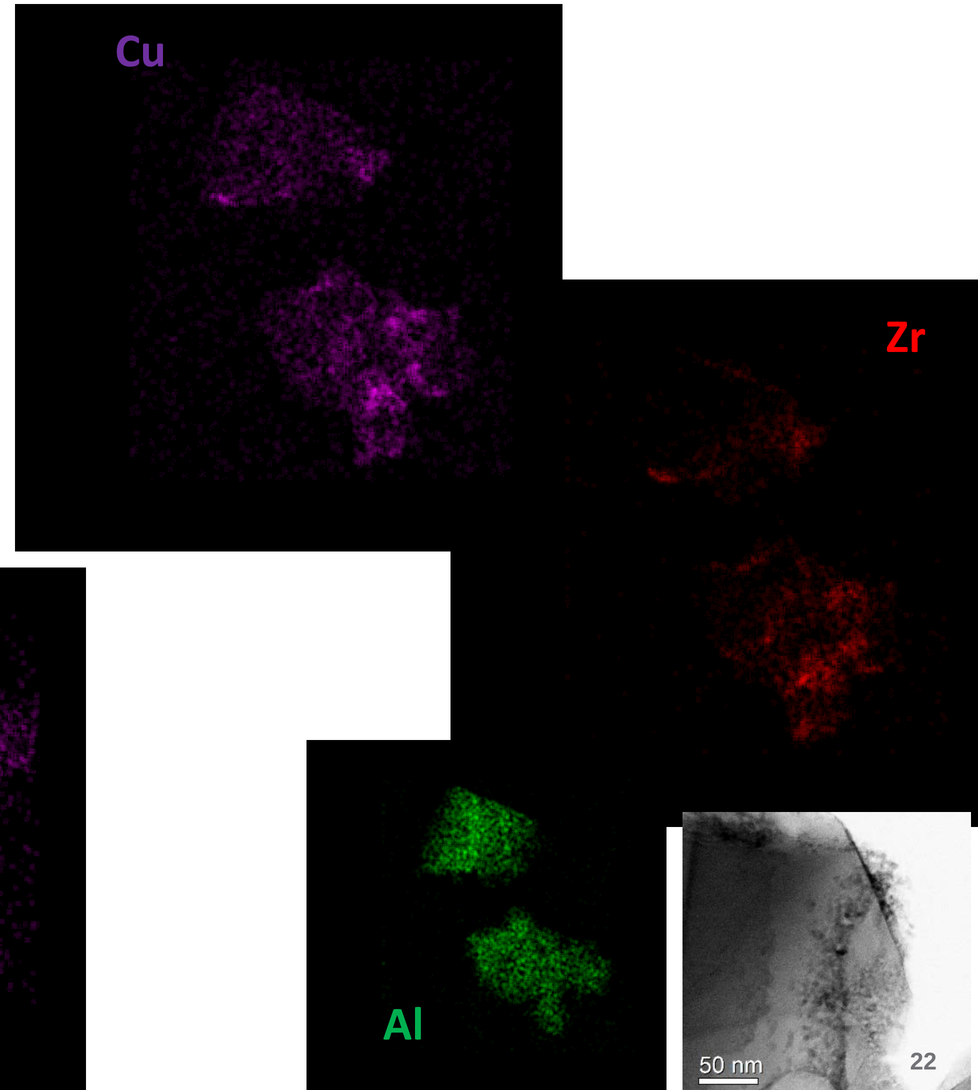
- Extra-framework Cu is predominantly responsible for the high temperature (400° C+) NH_3 oxidation activity.
- ***NH_3 oxidation directly affected by the generation of a new species resulting from the interaction between extra-framework Cu and ZrO_2.***

Backup – (S)TEM-EDS observed Cu-enrichment of ZrO_2

- Cu-CHA + ZrO_2 (deposited)



- Cu-CHA + ZrO_2 (impregnated)

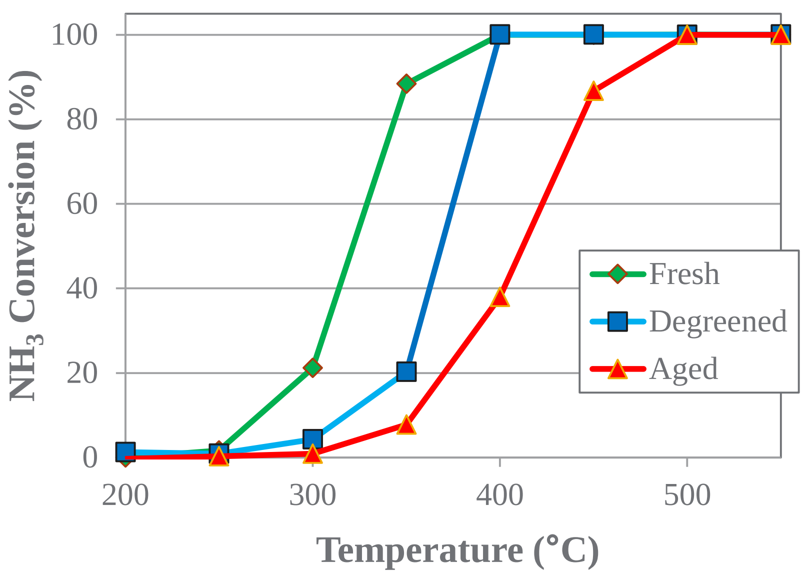


Backup – Model system study

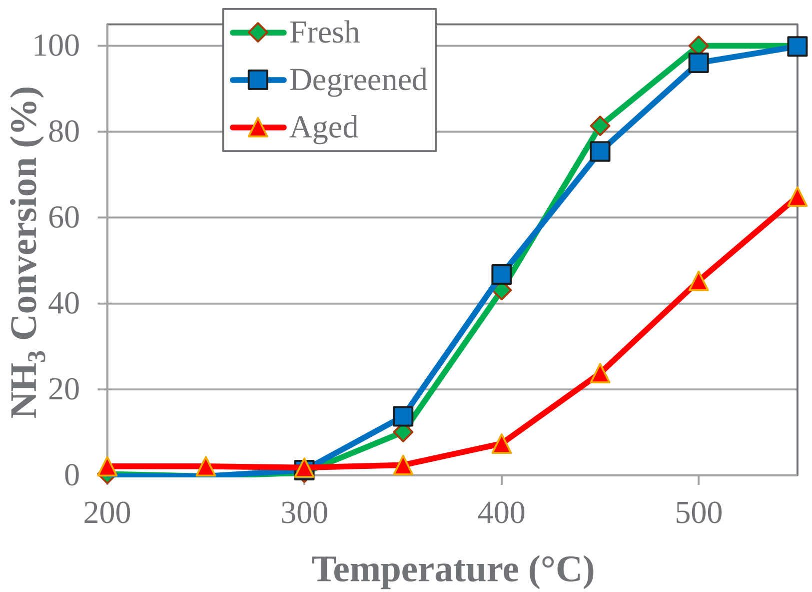
Pacific Northwest NATIONAL LABORATORY

- Intent of model catalyst is to mimic the interaction between extra-framework Cu (responsible for enhanced high temperature NH_3 oxidation) and ZrO_2. Inert SiO_2 is used as an inert substitute for Cu-CHA.

Catalyst 1: Cu impregnated on ZrO_2, then physical mixed with SiO_2



Catalyst 2: Cu and ZrO_2 simultaneously impregnated on SiO_2



Conditions: 360 ppm NH_3, 14% O_2, 2.5% H_2O, balanced by N_2, total flow rate 300 mL min^{-1}, 120 mg catalyst.

- *A close vicinity between Cu and ZrO_2 is necessary for reduced NH_3 oxidation activity and inducing the interaction between extra-framework Cu and ZrO_2.*

Backup – Understanding BaO/ZrO$_2$ aging

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

- *Aged* – 800°C/16 hours
- Comparing to aging at 650°C/100-hrs
  - *Significantly different at low temperature*
  - *Very similar at high temperature*

Confirms aging mechanism is unique, and NOT simply a propagation of conventional Cu-CHA aging

- 90% SCR + 10% Ba/Zr oxide